



Designation: D6729 – 20

Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography¹

This standard is issued under the fixed designation D6729; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of individual hydrocarbon components of spark-ignition engine fuels and their mixtures containing oxygenate blends (MTBE, ETBE, ethanol, and so forth) with boiling ranges up to 225 °C. Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates, and so forth) may also be analyzed; however, statistical data was obtained only with blended spark-ignition engine fuels.

1.2 Based on the cooperative study results, individual component concentrations and precision are determined in the range of 0.01 % mass to approximately 30 % mass. The procedure may be applicable to higher and lower concentrations for the individual components; however, the user must verify the accuracy if the procedure is used for components with concentrations outside the specified ranges.

1.3 The test method also determines methanol, ethanol, t-butanol, methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), t-amyl methyl ether (TAME) in spark ignition engine fuels in the concentration range of 1 % mass to 30 % mass. However, the cooperative study data provided sufficient statistical data for MTBE only.

1.4 Although a majority of the individual hydrocarbons present are determined, some co-elution of compounds is encountered. If this test method is utilized to estimate bulk hydrocarbon group-type composition (PONA) the user of such data should be cautioned that some error will be encountered due to co-elution and a lack of identification of all components present. Samples containing significant amounts of olefinic or naphthenic (for example, virgin naphthas), or both, constituents above *n*-octane may reflect significant errors in PONA type groupings. Based on the gasoline samples in the inter-

laboratory cooperative study, this procedure is applicable to samples containing less than 25 % mass of olefins. However, some interfering coelution with the olefins above C₇ is possible, particularly if blending components or their higher boiling cuts such as those derived from fluid catalytic cracking (FCC) are analyzed, and the total olefin content may not be accurate. Caution should also be exercised when analyzing olefin-free samples using this test method as some of the paraffins may be reported as olefins since analysis is based purely on retention times of the eluting components.

1.4.1 Total olefins in the samples may be obtained or confirmed, or both, if necessary, by Test Method **D1319** (percent volume) or other test methods, such as those based on multidimensional PONA type of instruments (Test Method **D6839**).

1.5 If water is or is suspected of being present, its concentration may be determined, if desired, by the use of Test Method **D1744**, or equivalent. Other compounds containing oxygen, sulfur, nitrogen, and so forth, may also be present, and may co-elute with the hydrocarbons. If determination of these specific compounds is required, it is recommended that test methods for these specific materials be used, such as Test Methods **D4815** and **D5599** for oxygenates, and **D5623** for sulfur compounds, or equivalent.

1.6 **Annex A1** of this test method compares results of the test procedure with other test methods for selected components, including olefins, and several group types for several interlaboratory cooperative study samples. Although benzene, toluene, and several oxygenates are determined, when doubtful as to the analytical results of these components, confirmatory analyses can be obtained by using specific test methods.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.04.0L** on Gas Chromatography Methods.

Current edition approved June 1, 2020. Published October 2020. Originally approved in 2001. Last previous edition approved in 2014 as D6729 – 14. DOI: 10.1520/D6729-20.

*A Summary of Changes section appears at the end of this standard

1.9 This international standard was developed in accordance with internationally recognized principles on standardization established in the *Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee*.

2. Referenced Documents

2.1 ASTM Standards:²

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

D1744 Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent (Withdrawn 2016)³

D4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography

D5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection

D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection

D6839 Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions*—This test method makes reference to many common gas chromatographic procedures, terms, and relationships. Detailed definitions can be found in Practice **E355**.

4. Summary of Test Method

4.1 Representative samples of the petroleum liquid are introduced into a gas chromatograph equipped with an open tubular (capillary) column coated with the specified stationary phase. Helium carrier gas transports the vaporized sample through the column, in which it is partitioned into individual components which are sensed with a flame ionization detector as they elute from the end of the column. The detector signal is recorded digitally by way of an integrator or integrating computer. Each eluting component is identified by comparing its retention time to that established by analyzing reference standards or samples under identical conditions. The concentration of each component in mass percent is determined by normalization of the peak areas after correction of selected components with detector response factors. The unknown components are reported individually and as a summary total.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

5. Significance and Use

5.1 Knowledge of the specified individual component composition (speciation) of gasoline fuels and blending stocks is useful for refinery quality control and product specification. Process control and product specification compliance for many individual hydrocarbons may be determined through the use of this test method.

6. Apparatus

6.1 *Gas Chromatograph*, a gas chromatograph equipped with cryogenic column oven cooling and capable of producing repeatable oven ramps from 0 °C to at least 300 °C is required. The following features are useful during the sample analysis phase: electronic flow readout, electronic sample split-ratio readout, and electronic pneumatic control of flow. Though their use is not required, careful review of this test method will demonstrate the usefulness of a gas chromatograph equipped with these features. These features will replace the need to carry out the manual calculations that must be performed as listed in **8.1** and **8.2**.

6.2 *Inlet*—a capillary split/splitless inlet system operated in the split mode is recommended. It must be operated in its linear range. Refer to **8.4** to determine the proper split ratio.

6.2.1 *Carrier Gas Pneumatic Control*—Constant carrier gas pressure control was used by all cooperative study participants. This may be either direct pressure to the inlet (injector) or by using a total flow/back pressure system.

6.2.2 *Pneumatic Operation of the Chromatograph*—The use of constant pressure was the mode of operating the gas chromatography used by the participants in the interlaboratory cooperative study. Other carrier gas control methods such as constant flow (pressure programming) may be used, but this may change the chromatography elution pattern unless the temperature programming profile is also adjusted to compensate for the flow differences.

6.2.3 *Temperature Control*—The injector operated in the split mode shall be heated by a separate heating zone and heated to temperatures of 200 °C to 275 °C.

6.3 *Column*, a fused silica capillary column, 100 m in length by 0.25 mm inside diameter, coated with a 0.5 µm film of bonded dimethylpolysiloxane. The column must meet the resolution requirements expressed in **8.3**. Columns from two different commercial sources were used in the interlaboratory cooperative study.

6.4 *Data System*, a computer based chromatography data system capable of accurately and repeatedly measuring the retention time and areas of eluting peaks. The system shall be able to acquire data at a rate of at least 10 Hz. Although it is not mandatory, a data system which calculates column resolution (R) is extremely useful as it will replace the need to carry out the manual calculations which must be performed as listed in **8.3**.

6.4.1 *Electronic Integrators*, shall be capable of storing up to 400 components in the peak table and shall be able to acquire the data at 10 Hz or faster speeds. They shall be capable of integrating peaks having peak widths at half height which are 1.0s wide. The integrator must be capable of

displaying the integration mode of partially resolved peaks. In addition, these integrators should be able to download a commonly readable format of data (that is, ASCII) to a computer in order to facilitate data processing.

6.5 Sample Introduction—Sample introduction by way of a valve, automatic injection device, robotic arm or other automatic means is highly recommended. An automatic sample introduction device is essential to the reproducibility of the analysis. Manual injections are not recommended. All of the reproducibility data reported by this test method for the samples analyzed were gathered using automatic injection devices.

6.6 Flame Ionization Detector (FID)—The gas chromatograph should possess a FID having a sensitivity of 0.005 coulombs/g for *n*-butane. The linear dynamic range of the detector should be 10⁶ or better. The detector is heated to 300 °C.

7. Reagents and Materials

7.1 Calibrating Standard Mixture—A spark ignition engine fuel standard of known composition and concentration by mass can be used. In order to corroborate the identification of the sample, a typical chromatogram (Fig. 1) was obtained from reference sample ARC96OX.⁴

7.2 Gas Chromatograph Gases—All of the following gases shall have a purity of 99.999 % (V/V) or greater.

NOTE 1—Warning: Gases are compressed. Some are flammable and all gases are under high pressure.

7.2.1 Helium—The test data was developed with helium as the carrier gas. It is possible that other carrier gases may be used for this test method. At this time, no data is available from this test method with other carrier gases.

7.2.2 Air, Hydrogen and Make-up Gas (Helium or Nitrogen), shall have a purity of 99.999 % (V/V) or greater.

8. Instrument Check Out Prior to Analysis

8.1 Setting:

8.1.1 Linear Gas Velocity—If the gas chromatograph is equipped with an electronic flow readout device, set the flow to 1.8 mL/min. This is achieved by setting the carrier gas flow rate by injection of cm/s methane or natural gas at 35 °C. Ensure that the retention time is 7.00 min ± 0.05 min. This corresponds to a linear velocity of 25 cm/s to 26 cm/s. This is equivalent to retention times of methane at 0 °C ranging from 6.5 min to 6.8 min.

8.1.2 If the gas chromatograph is not equipped with an electronic flow readout device, calculate the linear gas velocity in cm/s using Eq 1.

$$\text{linear gas velocity} = V = \frac{\text{column length (cm)}}{\text{retention time of methane(s)}} \quad (1)$$

⁴ Reference spark ignition sample No. ARC 960X obtained from the Alberta Research Council, Edmonton, Alberta, Canada. Other samples are available from suppliers.

8.1.3 The typical retention times for methane and linear gas velocity for helium are 6.5 cm/s to 6.8 cm/s and 24 cm/s to 26 cm/s, respectively.

8.2 Setting the Split Ratio—If the gas chromatograph is equipped with an electronic split-ratio readout device, set the split ratio to a sample split of 200:1. If the gas chromatograph is not equipped with an electronic split-ratio readout device, one must first calculate column flow rate and then proceed to calculating split ratio using Eq 2 and 3.

$$\text{column flow rate} = F = \frac{(60 \pi r^2) L(T_{ref}) 2(P_i - P_o)}{(T)3(P_{ref})(P_i^2 - P_o^2)\mu} \quad (2)$$

where:

F = flow rate as calculated by using the equation,
r = column radius, cm,
L = column length, cm,
P_i = inlet pressure,
P_o = outlet pressure,
P_{ref} = reference pressure, 1 atm,
T = temperature of the column oven,
T_{ref} = temperature at the column outlet, and
μ = linear velocity, cm/s.

$$\text{split ratio} = S = \frac{\text{split vent flow} + F}{F} \quad (3)$$

8.2.1 The column flow rate is calculated by the use of Eq 2. Use the results obtained from Eq 3 to adjust the split flow until a split flow of approximately 200:1 is achieved.

8.3 Evaluation of Column Performance:

8.3.1 Prior to using the column described in Table 1, measure the resolution of the column under the conditions of Table 2. Check that the resolution for the following pairs of components is obtained using Eq 4 to calculate the resolution of a pair of components:

$$R = \frac{2(t_{R2} - t_{R1})}{1.699(W_{h1} + W_{h2})} \quad (4)$$

where:

R = resolution,
t_{R2} = retention time of the first member of the pair,
t_{R1} = retention time of the second member of the pair,
W_{h1} = peak width at half height of the first member of the pair, and
W_{h2} = peak width at half height of the second member of the pair.

8.3.1.1 Column resolution should be checked frequently by examining the resolution of these compounds.

8.3.2 Evaluation of the Baseline—Carry out a blank baseline run utilizing no solvent injection, by setting the GC in accordance with the conditions of Table 1.

8.3.3 Subtract the baseline from a sample chromatogram and verify that the residual signal at the beginning of the chromatogram does not differ from the end of the chromatogram by more than 2 %.